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Original Article

Synthesis of FeNi-Ceramic composite by carbothermal reduction from Fe_2O_3-WO_3-Ni system

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Abstract

FeNi-Ceramics (Fe_3W_3C, Fe_6W_6C) composite powder was synthesized by carbothermal reduction of Fe_2O_3-WO_3-Ni mixture under argon gas atmosphere at 1200°C temperature. The standard Gibbs energy minimization method was used to calculate the equilibrium composition of the reacting species. Effects of synthesis milling time of precursors on the FeNi-Ceramics conversion were investigated. The resulted product phases and morphologies were identified using XRD and SEM methods. The synthesized products showed composite of ceramic (Fe_3W_3C, Fe_6W_6C) and iron-nickel alloy (FeNi) phases.

Keywords: carbothermal reduction, standard Gibbs energy minimization method, Fe_3W_3C, Fe_6W_6C, composites

1. Introduction

Metal matrix composites (MMC) have many advantages over monolithic metals including higher specific modulus, higher specific strength, and better wear resistance. Because of these attributes MMC are under consideration for a wide range of applications such as wear parts and cutting tools (Ross, 2006).

The prominent MMCs widely used by industries are WC-Co, WC-Fe and WC-Fe alloy systems. Fe-WC composites produced by direct mix of Fe and WC powders, are relatively expensive (Bennett and Jagner, 2005). Moreover, there are some difficulties to disperse reinforced particles of WC evenly in the Fe matrix. From these reasons many synthesis routes to produce Fe-WC were studied and proposed such as the self-propagating high temperature synthesis (SHS) (Jiang *et al.*, 2005; Jiang *et al.*, 2003; Mas-Guindal *et al.*, 2006; Nersisyan *et al.*, 2005; Saidi, 1999), and the carbothermal reduction of ilmenite (Niyomwas, 2005; Niyomwas, 2006) and tungsten oxide (Yang *et al.*, 2004; Koc, 2000).

In this study, a thermodynamic model for carbothermic reduction of Fe_2O_3-WO_3-Ni was developed. The experimental results of the synthesis of FeNi-ceramic composites were compared with the model calculations. An excellent agreement between model results and experimental data from this study was obtained.

2. Experiment

2.1 Raw Materials and experimental setup

Iron oxide powder (Fe_2O_3; 4.861 mm, 97%, RiedeldeHaën), tungsten oxide powder (WO_3; 1.005 mm, 99.9%, Fluka), activated carbon powder (C; 24.21 mm, 99%, sd finechem) and nickel powder (Ni; -100 mesh, 99.99%, Sigma-Aldrich) were used as the precursors. SEM micrographs of these precursors are presented in Figure 1

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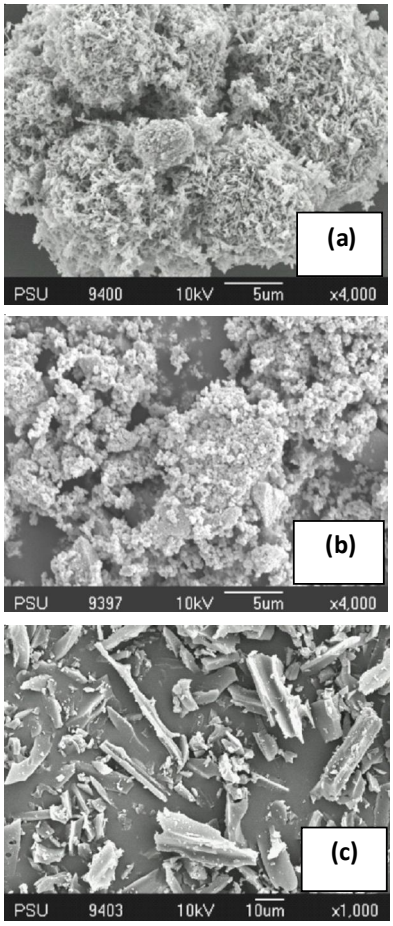

Figure 1. SEM micrographs of precursors : (a) Fe_2O_3 (b) WO_3 (c) activated carbon

The experimental setup is shown in the Figure 2. A tube furnace (Carbolite, CTF 18/75/600) with a maximum working temperature of 1800°C was used in the experiments. The in-situ reaction was performed in an alumina crucible, located in a furnace tube with one end connected to Ar gas supply system and another end partially open. Before heating, the furnace tube was evacuated and flushed with pure Ar gas for 2-3 times to remove O_2 and moisture. Then, pure Ar gas was introduced at a constant rate (3 LPM) to the furnace throughout the experimental process to maintain an inert atmosphere. An opening in the furnace end cover serves as the exit for gas. However, gases in the environment cannot enter the system due to the small pressure difference maintained by the flowing Ar gas.

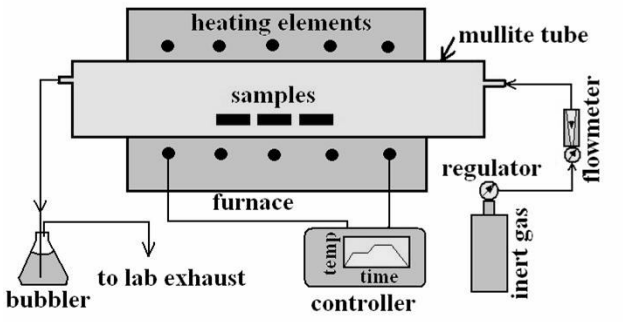

Figure 2. Schematic of the experimental setup

2.2 Experimental procedure

Iron oxide, tungsten oxide, activated carbon and nickel were weighted as stoichiometric molar ratio (Fe_2O_3/WO_3/C/Ni = 0.5/1.0/5.5/1.0) and milled in planetary ball-milled with a speed of 250 rpm and at milling time of 2, 12, 24 and 36 hours. This mixed powder was loaded into an alumina crucible placed in the middle of the tube furnace. The furnace was heated in a programmed manner from room temperature to 1200°C with a heating rate of 10°C $min^{-1}$and held at the final temperature for 1 h, then the furnace was turned off, allowing the product to cool in the furnace. The product powders were characterized using XRD (PHILIPS with Cu Ka radiation) and SEM (JEOL, JSM-5800 LV) analyses.

2.3 Thermodynamic analysis

Thermodynamic equilibrium calculations were performed using a computer program based on the Gibbs energy minimization method to determine the most stable compositions of the materials as a function of temperature. This method is based on the fact that systems will achieve equilibrium at the lowest possible energy level. Hence, the total Gibbs energy for a system is at a minimum at equilibrium. The equilibrium composition and distribution for the system Fe_2O_3-WO_3-Ni-C was calculated. This method is represented by equation (1) (Gokcen and Reddy, 1996):

$$G = \sum_{gas} n_i\left(g_i^o + RT\ln P_i\right) + \sum_{\substack{pure\\condensed\\phase}} n_i g_i^o + \sum_{solution} n_i\left(g_i^o + RT\ln x_i + RT\ln\gamma_i\right) \quad (1)$$

where, G is the total Gibbs energy of the system; g_i^o is the standard molar Gibbs energy of species i at P and T; n_i is the molar number of species i; P_i is the partial pressure of species i; x_i is the mole fraction of species i; and g_i is the activity coefficient of species i.

A mixture of Fe_2O_3-WO_3-Ni-C, annealed under argon gas atmosphere at the temperature of 1200°C, showed the formation of FeNi-WC. The overall chemical reaction can be expressed as:

$$0.5Fe_2O_{3(s)} + WO_{3(s)} + 5.5C_{(s)} + Ni_{(s)} \rightarrow FeNi_{(s)} + WC_{(s)} + 4.5CO_{(g)} \quad (2)$$

The equilibrium compositions of Fe_2O_3-WO_3-Ni-C system at different temperatures were calculated using Gibbs energy minimization method and the results are shown in Figure 3.

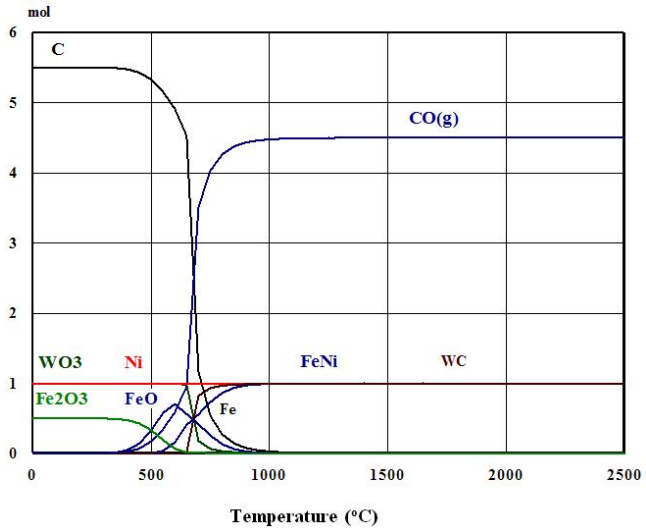

Figure 3. Gibbs energy minimization plots of Fe_2O_3-WO_3-Ni-C system in an argon atmosphere.

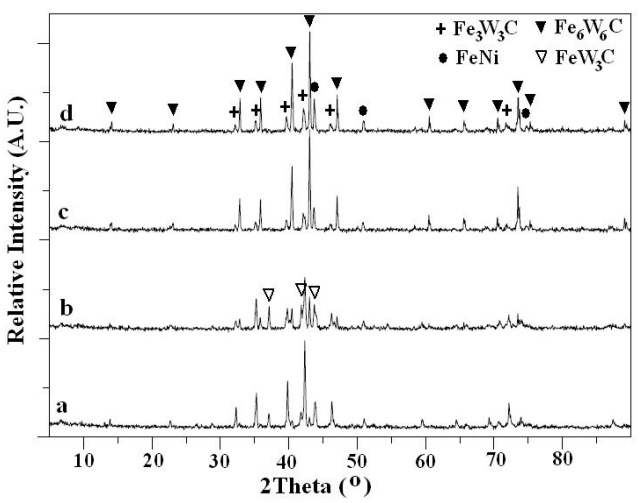

Figure 4. XRD pattern of product from the reduction temperature at 1200°C under Ar gas atmosphere of the precursors at different milling times (a =2 hr., b =12 hr.,c = 24 hr. and d =36 hr.)

3. Results and Discussion

3.1 Effect of milling time to the synthesis products of composites

All the synthesized experiments had carbothermal reaction and produced FeNi alloy and carbide phases of FeW_3C, Fe_3W_3C and Fe_6W_6C as shown in Figure 4. Figure 5 shows that Fe_3W_3C is the most stable phase when milling time used is 2 hr, and decreases with increasing milling time. On the other hand, Fe_6W_6C did not form at the precursor milling time of 2 hr and increases with increasing milling time. FeW_3C appeared in the product only at the lower milling time which may be explained from the reasoning that it was an intermediate phase of Fe_6W_6C. The phase transformations of carbides were resulting from the mixing homogeneity, the intimate contact and the activated state of the precursor particles that were finely ground by ball milling. These results agree well with an early study on formation of ternary carbide from Fe/W/C by Tsuchida *et al.*, 2001. The mechanisms of phase transformation of these carbides and intermediate phases may be written as:

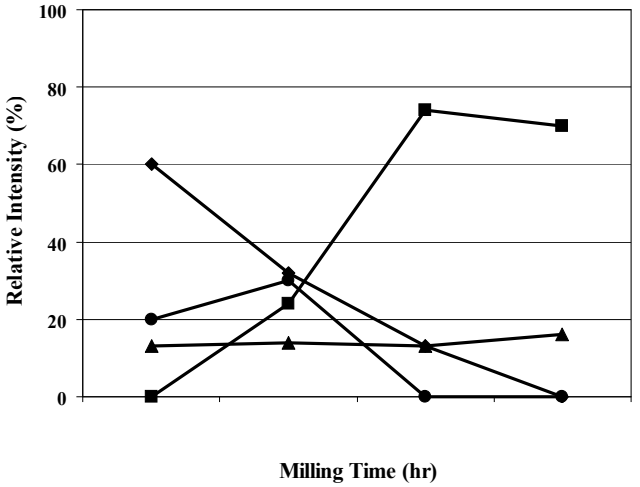

Figure 5. Relative Intensity of phases in synthesized products from the reduction temperature at 1200°C and the precursors at different milling times

$$FeW_3C_{(s)} + 2Fe_{(s)} \rightarrow Fe_3W_3C_{(s)} \quad (3)$$

$$2FeW_3C_{(s)} + 4Fe_{(s)} \rightarrow Fe_6W_6C_{(s)} + C_{(s)} \quad (4)$$

$$2Fe_3W_3C_{(s)} \rightarrow Fe_6W_6C_{(s)} + C_{(s)} \quad (5)$$

$$Fe_{(s)} + Ni_{(s)} \rightarrow FeNi_{(s)} \quad (6)$$

The ternary ceramic of FeW_3C, Fe_3W_3C and Fe_6W_6C in the products' results are inconsistent with predictions from theoretical thermodynamics analyses of the same precursors which are based on the equilibrium conditions. This happened because of the lack of thermodynamic data of the ternary carbides phases. Although the computer program cannot show some species that are not included in the program database but from equilibrium conditions of the calculations we can get approximately what products and at which synthesized temperature for a particular system.

The product morphology obtained from SEM micrograph in Figure 6 shows good inter-particles cohesion within agglomerated particles. The effect of precursors milling time is clearly visible as inter-particles disperse more with increasing milling time. These implies that phases of the composite products can be manipulated using different precursors milling time at same synthesis condition.

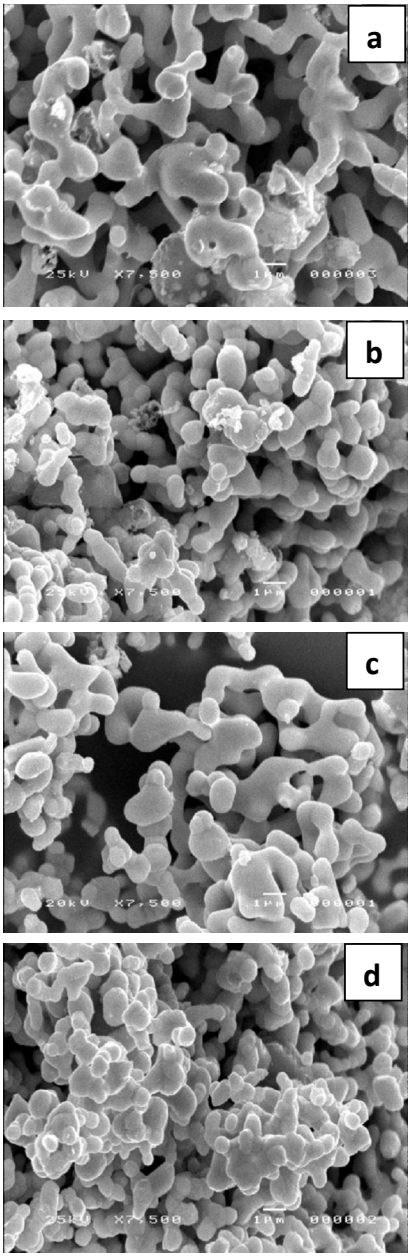

Figure 6. SEM micrograph of product morphology from the reduction temperature at 1200°C and the precursors at different milling time (a =2 hr., b =12 hr., c = 24 hr. and d = 36 hr.)

4. Conclusions

The *in-situ* synthesis of FeNi- carbides composite was produced via carbothermal reduction process at 1200°C from mixture of Fe_2O_3-WO_3-Ni. The product particles exhibited FeNi-(FeW_3C-Fe_3W_3C) phases when a precursor of 2 hr milling time was employed. At a precursor of 36 hr milling time, the resulted products were FeNi and Fe_6W_6C. The resulted products of FeNi-carbide composites show good inter-particles cohesion within the agglomerated particles.

Acknowledgements

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